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INFLUENCE OF SUBSTITUENTS IN CHLOROPOLYSTYRENES AND STYRENE COPOLYMERS ON THEIR THERMAL STABILITY

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The thermal properties of chloropolystyrenes and styrene copolymers were investigated by using TG and DTA methods. The chloropolystyrenes were obtained by chlorination of polystyrene (PS) with sulfuryl chloride in two ways: a) radical-initiation (products PR1-PR4, containing 15.7-48 wt. % of chlorine), b) ionic catalysis (product PI, containing 64 wt. % of chlorine). Thus, their structures were different. Three styrene copolymers were investigated too: poly(costyrene-phenyl maleimide) - PF, poly(co-styrene-o-chlorophenylmaleimide) - PCl, poly(co-styrene-p-hydroxyphenylmaleimide)–POH. The thermal stability of the polymers was higher when chlorine atoms were present on the aromatic ring.

The thermal stability of polymers is very important as regards both the range of their thermal application and also their non-burning properties. The burning of polymers occurs in two stages. Thermal decomposition of polymer occurs first, at higher temperature the products of decomposition burn in the gaseous phase [1]. Thus, it is very helpful to know the mechanism and products of the thermal decomposition of polymers, so as to define the most fire-resistant polymer structures and choose the way to obtain non-burning polymers.

In the present work we have studied this problem on polystyrene and its copolymers, due to their wide applications in many technical fields. Improvement of their thermal and nonburning properties is not only a scientific, but also a very important technical problem.

In previous work we have obtained and explored chloropolystyrenes containing chlorine atoms either on the aliphatic chain or on the aromatic rings. We have also worked on new styrene-maleimide copolymers. First the influence of the content and the position of the chlorine atoms in chloropolystyrenes on their thermal stability was investigated. The thermal stability was

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then compared with that of styrene copolymers with phenylmaleimide and its derivatives substituted with chlorine and hydroxyle groups on the aromatic rings. These studies have provided information on the dependence between the structures of the styrene polymers, the types and positions of the substituents in them, their thermal stability and, indirectly, their non-burning properties. They therefore give a guide to methods of modification of the styrene polymers as well.

Experimental

Samples

The samples used in this study:

a) Polystyrene PS ($\overline{M}_v$ = 46 000) was obtained by radical polymerization of styrene in benzene solution [2].

b) Chloropolystyrenes PR1-PR4, containing 15.7-48 wt.% of chlorine, were obtained by radical chlorination of PS with sulfuryl chloride in chlorobenzene solution [3].

c) Chloropolystyrene PI, containing 64 wt.% of chlorine, was obtained by ionic chlorination of polystyrene with sulfuryl chloride [4, 5].

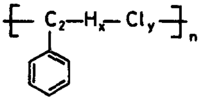
d) Three styrene copolymers: poly(co-styrene-phenylmaleimide) - PF, poly(co-styrene-o-chlorophenylmaleimide) - PCl, and poly(co-styrene-p-hydroxyphenylmaleimide) - POH, were obtained by the direct radical copolymerization of styrene and phenylmaleimide monomers containing substituted aromatic rings [6].

Instrument

The TG experiments were performed in the Department of Plastics and Rubber in the Technical University of Budapest, using a Paulik-Paulik C derivatograph under identical conditions, with a heating rate of 5 deg·min^{-1}, a sample mass of 20 mg and air atmosphere.

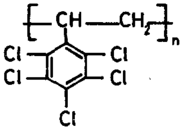
Results and discussion

To study the thermal stability of different polymer structures, we investigated polystyrene structures in which the substituents were on the aliphatic chain of the polymer, on the aromatic rings directly conjugated with the chain, and on the aromatic rings conjugated with the chain via the maleimide groups. The positions of the chlorine atoms in the chlorinated polystyrenes depend on the mechanism of chlorination. In the chloropolystyrenes obtained in radical-initiated reactions, the chlorine atoms were substituted on the aliphatic part of the polymer. The chlorine contents in these were: PR1 - 15.7 wt.% (0.54 Cl atoms/unit), PR2 - 27.0 wt. % (1.07 Cl atoms/unit), PR3 - 36 wt. % (1.62 Cl atoms/unit) and PR4 - 48 wt. % (2.62 Cl atoms/unit). The general formula of these is



PR1 - PR4
x = 3 - 0.38
y = 0.54 - 2.62

In the chloropolystyrene PI, obtained by the ionic chlorination of polystyrene with sulfuryl chloride in the presence of $AlCl_3$ and S_2Cl_2, the chlorine content was 64 wt. % and the chlorine atoms were substituted on the aromatic rings of the polystyrene. Almost all five positions (exactly 4.96) on the aromatic rings were substituted. The structure of PI is



PI

The TG, DTG and DTA traces of the studied chloropolystyrenes are illustrated in Fig. 1.

The thermal stabilities of PR1-PR4, in which the chlorine atoms are on the aliphatic part, are lower than that of polystyrene. The stability is the lowest when the polymer contains about 0.5 chlorine atoms per unit (PR1). Decomposition of this structure occures via a two-step mass loss from 240°.The weight loss during the first stage is about 17 wt. %. This suggests that this structure is subject to very ready dehydrochlorination.

With further increase of the chlorine content, the thermal stability of the chloropolystyrenes increases a little, and it is constant for the polymers in which the chlorine content is higher then 1 halogen atom per unit (PR2-PR4) (Fig. 2). This means that increase of the chlorine content above 27 wt. % does not influence the thermal stability of chloropolystyrenes containing chlorine atoms on the aliphatic part. For these structures, a two-step process of decomposition is not observed.

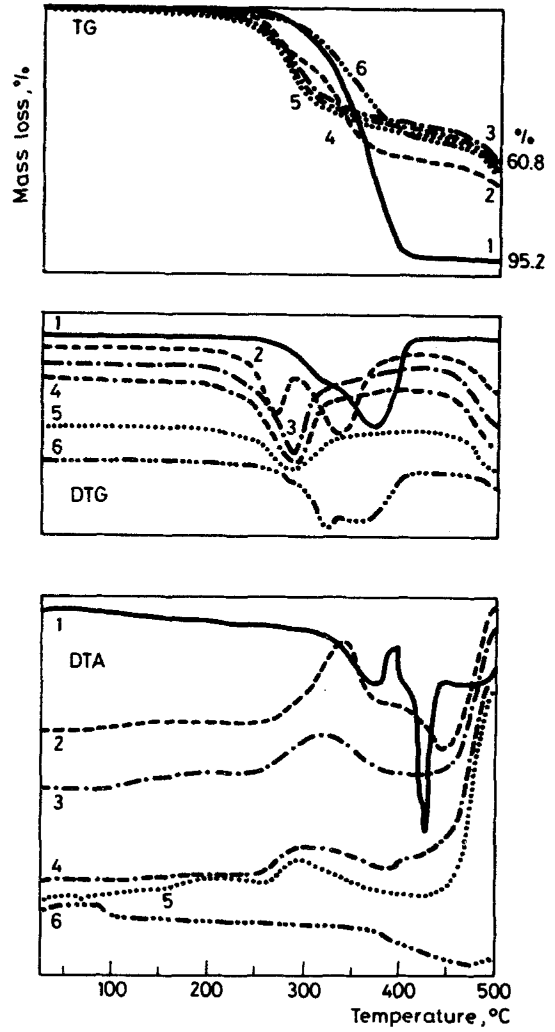


Fig. 1 TG, DTG and DTA curves for: 1 - polystyrene (PS) and chloropolystyrenes containing, 2 - 15.7 wt. % (PR1), 3 - 27.6 wt. % (PR2), 4 - 36.0 wt. % (PR3), 5 - 48.0 wt. % (PR4), 6 - 64.0 wt. % (PI) of chlorine

The thermal stability of chlorinated polystyrene increases very much when the chlorine atoms are substituted on the aromatic rings of the polymer (PI) (Fig. 2). It is even higher than the stability of polystyrene. The main peak of decomposition of this structure is detected at 340°.

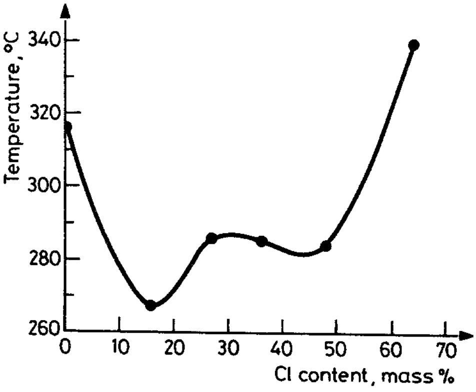
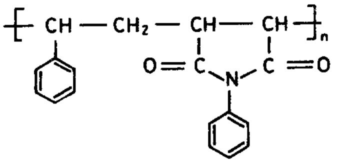


Fig. 2 Influence of chlorine content in chloropolystyrenes on the temperature of their decomposition

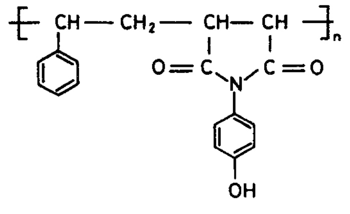
These data prove that the thermal stability of chloropolystyrenes depends on the chlorine content, but also very considerably on the structure of the polymer. Chloropolystyrenes containing chlorine atoms in the aliphatic part are less thermally stable than polystyrene, because of the very ready dehydrochlorination which occurs in these structures. However, this tendency shows the possibility of obtaining polystyrene semiconductors with a long conjugated double bond system. Chloropolystyrene containing 0.5 chlorine atoms per polymer unit would be especially suitable for this purpose.

The chloropolystyrene structure in which the chlorine atoms are on the aromatic rings is much more stable then polystyrene.

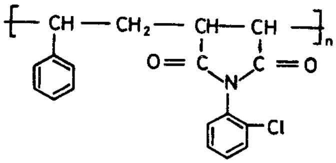
The same phenomenon is observed for the copolymers of styrene. We have investigated PF, PCl and POH, the structures of which are



PF



POH



PCl

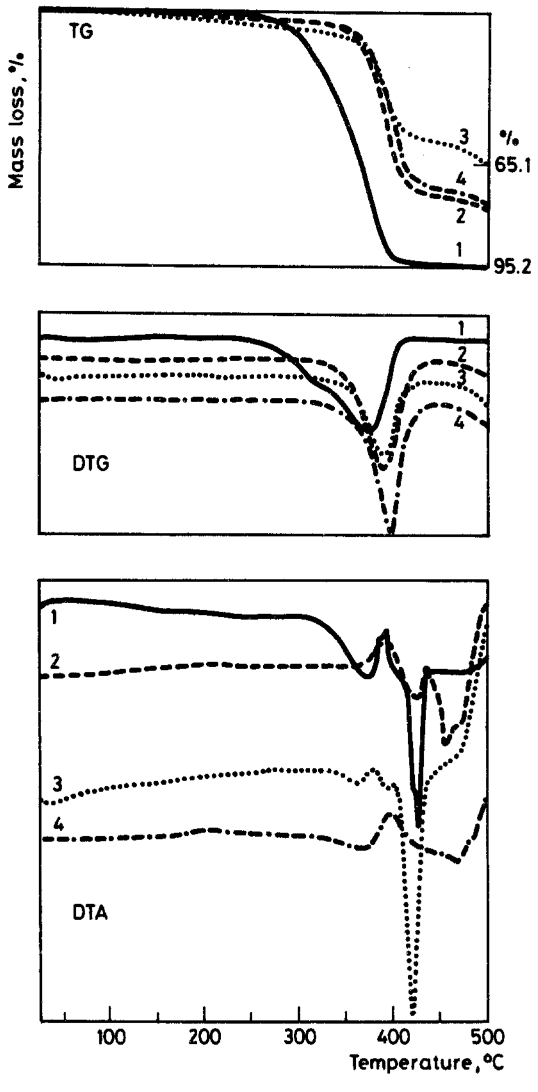


Fig. 3 TG, DTG and DTA curves for: 1 - polystyrene (PS), 2 - poly(co-styrene-phenylomaleimide) (PF), 3 - poly(co-styrene-o-chloro-phenylomaleimide) (PCl), 4 -poly(co-styrene-p- -hydroxyphenylomaleimide) (POH)

Figure 3 shows TG, DTG and DTA curves of polystyrene and these copolymers. The chlorine atom present on the aromatic ring in PCl elevates

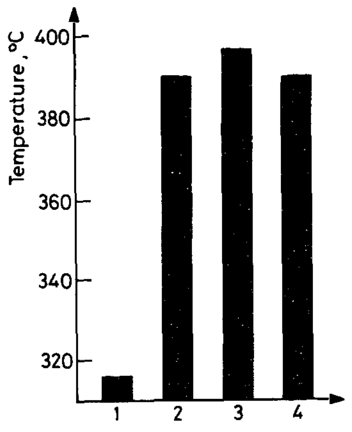


Fig. 4 Temperatures of decomposition of: 1 - polystyrene (PS), 2 - poly(co-styrene- -fenylomaleimide) (PF), 3 - poly(co-styrene-o-chloro-fenylomaleimide) (PCl), 4 - poly(co- -styrene-p-hydroxyphenylomaleimide) (POH)

the temperatures of the first thermal process and the decomposition of the copolymer. This does not occur when there is a hydroxy substituent on the aromatic ring (POH). The thermal stability of styrene-substituted phenylmaleimide copolymers is much higher than that of PS (Fig. 4). This indicates good ways to modify polystyrene to obtain new thermal and fire-resistant polymeric materials.

References

1 R. T. Sikorski, Proceeding of the Third Meeting on Fire Retardant Polymers, Italy, Torino, 21-22 September 1989, p. 81.
2 I. Losiew, O. Fedotova, Praktikum Po Chimii Vysokomolekularnyh Sojedinienij, Gozchimizdat, Moskva, 1962.
3 R. T. Sikorski, G. Mirkiewicz, to be published.
4 R. T. Sikorski, G. Mirkiewicz, European Polymer Journal, 24 (1988) 157.
5 G. Mirkiewicz, R. T. Sikorski, Patent Pl nr. 144807, 1986.
6 R. T. Sikorski, A. Puszynski, G. Mirkiewicz, Z. Izdebski, Raport SPR nr 11/1989, Instytut Technologii Organicznej I Tworzyw Sytucznych Politechniki Wroclawskiej, Wroclaw, 1989.

Zusammenfassung — Mittels TG- und DTA-Verfahren wurden die thermischen Eigenschaften von Chlorpolystyrolen und Styrolkopolymeren untersucht. Chlorpolystyrole wurden durch die Chlorierung von Styrol mittels Sulfurylchlorid auf zwei Wegen erhalten: a) durch radikalischen Kettenstart (Produkte PR1-PR4 mit 15.7-48 Massenprozent Chlor), b) durch ionische Katalyse (Produkt PI mit 64 Massenprozent Chlor). Die Strukturen sind somit verschieden. Es wurden auch drei Styrolkopolymere untersucht: Poly(co-styrol-phenylmaleinsäureimid) - PF, Poly(co-Styrol-o-Chlorphenylmaleinsäureimid) PCl, Poly(co-Styrol-p-Hydroxyphenylmaleinsäureimid) - OH. Durch die Einführung von Chloratomen am aromatischen Ring wächst die thermische Stabilität der Polymere.